FINAL REPORT

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“Electron Diffraction Determination of Nanoscale Structures”

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Introduction

The size-dependent evolutions of the structures and physical and chemical properties of finite nanoscale materials aggregates have been the subjects of continuing basic and applied research interests. Structure determination is one of the outstanding challenges of cluster science, and it has been approached in several ways. Structural determination via analysis of diffraction measurements is most desirable, since the scattering data is related to the spatial arrangement of the scattering atoms in a direct manner. However, until the initial measurements¹ that applied diffraction measurements to clusters structures such methodology was not practiced because of experimental technical difficulties, and consequently one resorted to more indirect methods, mostly through theoretical analysis of photoelectron spectroscopic (PES) data.²⁻⁵ Electron diffraction measurements, which may be regarded as a direct structural determination method,⁶ allow for a comparison between the experimentally measured data and theoretical calculations, insofar as the measured patterns are the Fourier transform of the pair correlation function and thus are directly related to atomic positions. Quite recently it has been demonstrated that trapped ion electron diffraction (TIED) measurements of mass selected metal clusters are particularly sensitive to changes in local order of silver cluster structures⁷ and size-dependent changes in the structural symmetries of gold clusters.⁸

Analysis of the electron diffraction data, including comparisons between the measured diffraction patterns and those calculated for theoretically optimized structures, is required in order to fully determine the atomic arrangement. Consequently, collaborations with theorists have provided essential contributions to this program. The success of combining TIED measurements with theoretical calculations to identify the structures of $(\text{Au}_n)^-$ suggested an approach to study adsorption processes of small molecules which are involved in the initial kinetics leading to nanocatalytic activity. It was identified by recent experimental and theoretical investigations of gold cluster anions that these species present a unique opportunity to correlate sizes and structures with catalytic reactivity on an atom-by-atom level. In these studies, relationships between cluster structures and catalytic activities have been explored for metal-oxide supported gold nanoclusters, and for gas-phase $(\text{Au}_n)^-$ clusters.⁹⁻¹² As a result, we proceeded to reorient our research emphasis to measure the gas phase adsorption of small gas phase molecules (O_2 , H_2O , CO) on gold cluster cations and anions using the structures determined by diffraction measurements as well as PES and ion mobility methods .

This document is the Final Report of our DOE program and as such I have decided it would be a valuable contribution to review the dominant research accomplishments in the adsorption on gold clusters which have been presented at DOE sponsored meetings¹³⁻¹⁵ but not yet published in scientific journals. The most important of these results are in preparation for submission to scientific journals over the next year. This change in research orientation provided an opportunity to investigate how the adsorption of small molecules on cluster ions depended on the cluster structure. Consequently the cluster adsorption research depends on cluster structures and as such is intimately linked to the diffraction research and theoretical calculations of these structures. This research program has been related to the DOE Electron and Scanning, Probe Microscopies (ESPM) Program in the Materials Science and Engineering Division mission by providing a method for confirming the design of nanosize materials at the atomic level; by providing an experimental tool for characterization of nanoscale phenomena; and by allowing a more complete understanding of nanoscale properties.

A. Adsorption of H₂O and O₂ on gold cluster cations and anions.

Based on the understanding of gold cluster structures, experimental and theoretical investigations of gold cluster anions present a unique opportunity to correlate sizes and structures with catalytic reactivity on an atom-by-atom level. This section describes the initial measurements which characterized the chemisorption of water and oxygen molecules on gold cluster anions and cations. The results clearly identified correlations between chemisorption reactions and cluster *structures*.

Adsorption measurements are performed by admitting the reactant gas into a quadrupole ion trap after a particular cluster ion size is mass selected and thermalized at the temperature of a background helium gas. The equilibrium product species, Au_nX_x⁻ and Au_nX_x⁺, are mass analyzed by ejecting the trapped product ions into a channeltron detector after long exposures to the reactant species.

A.1. Gold cluster anion complexes with oxygen

Figure 1 displays multiply adsorbed O₂ molecules at 150 K, p_{O2}=10⁻⁴ Torr, and exposure time of 50 s. Odd number sizes show weaker adsorption of only a single O₂. Best fit structures are shown for the two most strongly adsorbing cluster sizes at n=20 and 22. Beam experiments¹⁶ exhibited only singly adsorbed O₂ on even number sizes and identified correlation of the adsorption strength with electron affinity.

Figure 1. Multiply adsorbed O₂ molecules on gold cluster anions. Black rectangles indicate single O₂ molecule adsorption and blue rectangle indicates adsorption of 2 molecules. Insets show structures and enlarged mass spectra of $[\text{Au}_n(\text{O}_2)_x]^-$ complexes for $n=20$ and 22.

A.2. Theory for O₂ Adsorption on Au_n⁻ Clusters 7 ≤ n ≤ 26

Figure 2 displays a mass spectra of clusters which have been exposed to $p(\text{O}_2)=1 \times 10^{-4}$ Torr, for 50 s at 190 K. Equilibrium adsorption of a single oxygen molecule is indicated for $n=8,10,12,14,18,20$.

Figure 2. Mass spectrum of adsorbed O₂ molecules observed at 190K, $p(\text{O}_2)=10^{-4}$ Torr, for exposure time 50 s. Peaks corresponding to singly adsorbed O₂ are indicated by the solid circles.

Calculations performed were directed mainly at the determination of the structures and binding characteristics of oxygen molecules to anionic gold clusters. These explorations were performed using first-principles density functional theoretical calculations, using scalar relativistic pseudopotentials for the gold atoms (with 11 electrons per atom, $5d^{10}6s^1$, and an extra electron per cluster), and PBE generalized exchange correlation (GGA) corrections.

The structures of the gold cluster cations with $n=2-24$ atoms, and an adsorbed oxygen molecule were obtained. The energy-optimal structures were determined through energy minimization starting from the atomic arrangements determined in our previous investigations for the bare gold cluster anions.⁸ In all cases except for clusters with $n=11$ and 14 gold atoms, the oxygen molecule adsorbs forming a single bond directly to a gold atom of the clusters; for $n=11$ and 14 the two atoms of the oxygen molecule are bonded to neighboring Au atoms.

The corresponding binding energies of the oxygen molecule to the clusters, the interatomic O-O distance between the oxygen atoms, and the amount of excess electronic charge on the adsorbed molecule, along with the vertical detachment energy (vDE) of the extra electron from the bare gold cluster anion, are given in Figure 3.

As observed from Figure 3, the binding energies of the oxygen molecule to the gold cluster anti-correlate with the vDE values, with a high vDE corresponding to a small binding energy, while a low vDE value corresponds to a high binding energy. This trend reflects the fact that bonding of the molecule to the gold cluster anion involves partial transfer of an electron to the antibonding ($2\pi^*$) molecular orbital of the oxygen molecule. This trend is reflected also in the O-O bond length and the amount of excess electronic charge on the adsorbed molecule.

Figure 3. The vertical detachment energy (vDE), binding energy (BE), O₂ bond length d_{O-O} and excess charge (δQ) calculated for O₂ on Au_n.

Indeed, a high value of the binding energy corresponds to a larger O-O bond length compared to the gas-phase value, where d_{O-O} = 1.25 Angstroms; the larger bond length corresponds to a weakened inter-molecular bond, associated with an activated adsorbed molecule. Moreover, for clusters with a larger value of d_{O-O} we find also a larger amount of excess electron charge, corresponding to a larger occupation of the antibonding molecular orbital.

In most cases we find an even-odd alternation of the BE (O₂), which is reflected also in the other characteristic quantities (see Figure 3). In those cases where this alternating pattern is interrupted (see in particular the intervals n=9-12 and n=15-18), an explanation in terms of a “partial jellium” shell structure⁵ applies. In general, these calculations are consistent with the experimental mass spectra obtained for singly adsorbed O₂ (Figure 2).

A.3. Gold cluster cation and anion complexes with water.

Figure 4 displays a mass spectrum indicating that H₂O adsorption is occurring only on *planar* Au_n⁺ structures. The saturation number of adsorbed molecules is given in parentheses above the cluster structures. The spectrum is obtained at 298 K, p_{H₂O}=2×10⁻⁸ Torr, p_{He}=5×10⁻³ Torr, and exposure time of 20 s. All cation structures were obtained from Ref.17.

Figure 4. Mass spectrum indicates adsorption is occurring only on *planar* structures. The saturation number of adsorbed molecules is given in parentheses above the cluster structures. The spectrum is obtained at 298 K, p_{H₂O}=2×10⁻⁸ Torr, p_{He}=5×10⁻³ Torr, exposure time 20 s.

Figure 5 displays a mass spectrum indicating that H₂O adsorption is occurring only on *planar* Au_n⁻ structures for n=4,5, and 6. The saturation number of adsorbed molecules is 2 independent of cluster size. The spectrum is obtained at 298 K, p_{H₂O}=2.4×10⁻⁷ Torr, p_{He}=5×10⁻³ Torr, and exposure time of 20 s. All anion structures were obtained from Refs.8,12,18.

Figure 5. Mass spectrum of Au_n(H₂O)_x⁻ complexes. The structures shown up to n=11 are planar as shown by the structure insets. Next to each mass peak, the cluster size and number of H₂O molecules is indicated for the group of adjacent complexes.

These results for O₂ and H₂O complex formation on gold clusters indicate that the atomic structure plays a significant role in adsorption processes on metal clusters. These measurements have exhibited several very specific dependences on structure which are currently being pursued by calculations. The advantage of performing these measurements in gas phase is to ensure that the starting structure is well defined and can be determined by a combination of diffraction measurements and calculations. In this way, the possibility of identifying details of the adsorption process (and subsequent reactivity) can be realized.

B. Kinetics of CO adsorption to middle sized gold cluster cations.

Measurements of the formation kinetics of CO on Au_n^+ for $n = 8-10$ were performed for several reasons. As discussed in the Introduction, small gold clusters have been recognized for their fundamental importance as substrates in measurements of nano-catalysis. In addition, it was necessary to reproduce previous CO adsorption results by the Kappes group^{19,20} in order to calibrate the CO and He pressures and rates in our ion trap measurements. These measurements assured us of the accuracy expected in experiments planned to measure the saturation of CO adsorption and the co-adsorption of CO and H₂O on gold cluster cations.

Previous experiments¹⁹⁻²¹ of CO adsorption were performed in a Fourier Transform Ion Cyclotron Resonance (FT-ICR) trap in the absence of helium background gas. Our measurements utilize a quadrupole ion trap for which the helium pressure is required to stabilize the ions injected. This provides an opportunity to derive CO binding energies as a function of cluster size in a collisional environment and compare these energies with the FT-ICR results. The ion trap instrumentation and mass spectrometry measurements were similar to those described in Section A experiments.

The following discussion in Section B.1 will first describe the rate equation analysis used to extract the kinetic parameters from the experimental measurements. The data and kinetic rates will be shown in Section B.2.

B.1. Rate equations for kinetics analyses

The Lindemann Energy-Transfer Model leads to the following rate analysis of the kinetics for the CO adsorption on Au_n^+ :

$$\frac{d[M_n^+]}{dt} = -k_{\text{eff}}[X]t \quad \frac{d[M_n X^+]}{dt} = 0 \quad (3)$$

$$k_{\text{eff}} = \frac{k_a k_r}{k_d + k_r + k_c [\text{He}]} + \frac{k_a k_c [\text{He}]}{k_d + k_r + k_c [\text{He}]} \approx k_{\text{eff}}^{(2)} + k_{\text{eff}}^{(3)} [\text{He}] \quad (4)$$

The metal cluster cation is designated by M_n^+ and CO by X so that the complex is $[M_n X^+]$ and a vibrationally excited complex is shown by $[M_n X^+]^*$. The effective rate for the formation of a stable complex is shown as k_{eff} in Eqs.1,3 and defined in Eq.4. The 3 reactions contributing to the kinetics are shown in Eq.2(a,b,c) in which k_a is the ion-neutral collision rate (Langevin) depending on the CO polarizability; k_r is the radiative relaxation rate obtained using the single photon emission model; k_c is the ion-neutral collision rate depending on the helium

polarizability. The back rate, k_d is a unimolecular dissociation rate for the complex and is determined experimentally by the other rates as shown below. The binding energy of CO can be obtained from k_d using RRKM theory.

Eq.4 has been derived assuming the rates in Eq.3 are satisfied and the resulting net rate for the loss of the cluster cation population is observed to be composed of two terms. The first term in Eq.4 is due to bimolecular collisions, $k_{\text{eff}}^{(2)}$, in which relaxation of the excited state $[M_nX^+]^*$ occurs radiatively. In the second term, the stable complex formation rate, $k_{\text{eff}}^{(3)}$, occurs by termolecular collisions of both CO and helium with the cluster. This term expresses relaxation of the excited state by helium collisions.

B.1.1 Experimental determination of $k_{\text{eff}}^{(2)}$

In the limit that $[\text{He}] \rightarrow 0$, we have

$$k_{\text{eff}}^{(2)} = \frac{k_a k_r}{k_d + k_r} \approx \frac{k_a k_r}{k_d} \quad (5)$$

This limit has been used in the reactions of small molecules with clusters trapped within a FT-ICR in the absence of buffer gas. In particular, this limit has been used to determine CO binding energies by the Kappes group.¹⁹

B.1.2 Experimental determination of $k_{\text{eff}}^{(3)}$

In the limit $k_c [\text{He}] \gg k_r$, we have

$$k_{\text{eff}}^{(3)} = \frac{k_a k_c}{k_d + k_r + k_c [\text{He}]} \approx \frac{k_a k_c}{k_d} \quad (6)$$

which is readily achieved for vibrational radiative rates and helium background pressures in quadrupole ion traps. This limit has been used in the reactions of small molecules with clusters trapped within a quadrupole ion trap in the presence of buffer gas.²²⁻²⁶

B.2 Data acquisition and analysis

Data which describes the formation of $\text{Au}_{10}\text{CO}_n^+$ complexes is obtained by exposing trapped Au_{10}^+ clusters to CO at a constant helium background pressure for varying times. Mass spectra are obtained by ejecting the trapped ions into an ion detector. These spectra display the formation of complexes containing different numbers of CO molecules depending on the exposure time, the CO pressure and the helium pressure. In general the CO pressure is held constant, and the exposure time is varied for a set of helium pressures. An example of this data is shown in Figure 6. An exponential fit of the decay of the parent Au_{10}^+ clusters (Eq.3) yields a value of k_{eff} (Eq.4) for each helium pressure.

Figure 7 shows the analysis plot of k_{eff} vs helium pressure for Au_8^+ , Au_9^+ , and Au_{10}^+ clusters derived from the exponential fits. As indicated in Eqs.5 and 6, this analysis assumes that the back reaction rate, k_d , dominates the radiative rate, k_r , as well as the termolecular formation rate $k_c[\text{He}]$ for the vibrational radiation rate and the CO and helium pressures used in these measurements. Note that the plot of k_{eff} vs helium pressure indicates a linear fit which supports these assumptions. As a consequence, the intercept at $[\text{He}] = 0$ yields $k_{\text{eff}}^{(2)}$ and the slope of the linear fit yields $k_{\text{eff}}^{(3)}$. Note that the values for both $k_{\text{eff}}^{(2)}$ and $k_{\text{eff}}^{(3)}$ vary significantly for these 3 cluster cations suggesting dependence on the cluster structure vs size.

Figure 6. The panel on the left shows ion trap mass spectrometry data for the formation of complexes $\text{Au}_{10} \text{CO}_n^+$ following exposure of Au_{10}^+ to CO for varying times; and the panel on the right shows the fraction of each complex vs time derived from the mass spectra intensities.

Figure 7. A plot of k_{eff} vs helium pressure is shown for each parent Au_n^+ cluster with $n=8,9,10$.

The values of $k_{\text{eff}}^{(2)}$ and $k_{\text{eff}}^{(3)}$ determined by these analyses are shown in Table 1. The values of $k_{\text{eff}}^{(2)}$ for $\text{Au}_n^+(n=8-10)$ agree within experimental error for those previously reported.¹⁹ Gold anions have extremely low reaction rates with CO at room temperature. The cluster size Au_{11}^- yields the only rate that lies within the measurement window of our instrument.²⁶ The value of $k_{\text{eff}}^{(2)}$ for Au_{11}^- are slightly lower than reported previously.²¹

Table 1. Values of $k_{\text{eff}}^{(2)}$ and $k_{\text{eff}}^{(3)}$

Cluster	$k_{\text{eff}}^{(2)}$ 10-12 cm³/s	$k_{\text{eff}}^{(3)}$ 10-22 cm⁶/s
Au_8^+	1.33±0.17	0.59±0.04
Au_9^+	0.51±0.23	0.49±0.04
Au_{10}^+	2.59±0.15	1.39±0.06
Au_{11}^-	0.23±0.21	0.048±0.006

B.3 Calculation of the binding energies for CO on Au_n^+

RRKM calculations are planned to calculate the values for k_d to identify the binding energy (BE) which yields the closest comparison with experimentally determined k_d values. Note that k_d has been used¹⁹ for this purpose in measurements relying on radiative relaxation (Eq.6). By utilizing Eq.6, we can also find the BE for the case of collisional relaxation to identify differences. Density functional calculations are in progress to determine the structure and vibrational frequencies for the $\text{Au}_n \text{CO}^+$ complexes required for the RRKM calculations.

C. Adsorption of CO on Au_n^+ : induced changes in structure.

It is generally understood²⁷ that the reactivity dependence on cluster size is actually expressing a dependence on cluster structure which is evolving with size. Establishing the correlation between cluster adsorption and cluster structure is essential for understanding mechanisms giving rise to observed reactivity.^{9,28} Gas phase measurements provide an opportunity to investigate relationships between cluster structure and reactivity unperturbed by surface interactions. Such measurements can be reliably modeled^{8,17,29} by DFT calculations.

The adsorption of CO on Au_n^+ for $n=3-20$ exhibits induced changes in cluster structure for many of the sizes studied. An example of this can be observed in the mass spectra of Au_{10}^+ shown in Figure 8.

Figure 8. Mass spectra for CO adsorption on Au_{10}^+ . The cluster size and saturation number of adsorbed molecules is given in parentheses (n,m). These spectra were obtained at the pressures, temperatures and exposure times indicated on the right. Cation structures were obtained from Ref.6. Note that the mass spectrum at 300 K, $4.8\text{E-}6$ Torr and 5 s exhibits the coexistence of both 2D and 3D structures in the cluster ensemble. Additional uptake of CO to 8 molecules only occurs at the lower temperature

Figure 8 shows mass spectra for CO adsorption on $\text{Au}_{10}(\text{CO})_m^+$ for $m \leq 8$. These spectra indicate that adsorption begins on the 3D ground state structure of the bare gold cluster and achieves saturation at $m=8$ only after transitions to a 2D structure. The abrupt changes in the spectra are consistent with the structural changes indicated. Saturation at $m=8$ is achieved only at reduced temperature of 150 K.

In an effort to identify how this structural change occurs, calculations were carried out for a more manageable complex, $\text{Au}_6(\text{CO})_3^+$. Calculations were performed for Au_6^+ to investigate the changes in structure induced by the adsorption of CO between the ground state triangular structure and a low energy isomer having a chevron structure. Figure 9 illustrates changes in the transition energy barrier between the two isomers as well as the change in relative energy between the initial and final structures.

Figure 9. This schematic displays the results of DFT calculations for the structural transformation of Au_6^+ induced by CO adsorption. Panel (a) shows the energetics for a transition between two structural isomers for the bare cluster cations and panel (b) for the cluster with 3 adsorbed CO molecules.

Figure 9 indicates that the adsorption of three CO molecules on the chevron isomer occurs with stronger binding energy than on the triangular isomer. This adsorption decreases the energy of the chevron structure to 0.24 eV below that of the triangular structure energy. More importantly, the energy barrier for a structural transition is reduced to roughly half the cluster internal energy at 300 K. As a result, a structural transition becomes significantly more probable with the adsorption of 3 covalently bound CO molecules. This calculation of the structural transformation of Au_6^+ suggests a characteristic energetic pathway leading to transformations inferred by the data in Figure 8.

D. H₂O enhancement of CO adsorption

During measurements of CO adsorption on Au_n⁺, it was observed that for certain sizes the change in saturation number was accompanied by the co-adsorption of H₂O molecules. Measurements were performed to determine if the co-adsorption of H₂O and CO systematically leads to increased CO uptake. In these measurements, the cluster is exposed to the H₂O vapor pressure first followed by exposure to CO. The presence of H₂O strongly influences the adsorption of CO on Au₆⁺; however, *adsorbed H₂O is not observed* suggesting that the enhancement does not require H₂O to remain stabilized on the cluster surface. Calculations were performed to understand the dynamics of these observations.

Figure 10 indicates that the presence of H₂O strongly increases the adsorption rate of CO on Au₆⁺ by a factor of ~17. However, adsorbed H₂O is not observed in the mass spectra suggesting that the rate enhancement does not require H₂O to remain stabilized on the cluster surface after CO adsorption.

Figure 10. Mass spectra of (a) the adsorption of CO on Au₆⁺ in the presence of background water vapor and (b) the co-adsorption of H₂O and CO on Au₆⁺ vs exposure time for p(He)=3.5E-3 Torr, 300K. The numbers indicate the number of CO molecules for each mass peak.

Figure 11. Calculated energetic pathways to describe the H₂O enhancement shown in the data of Figure 4.

The schematic in Figure 11 displays the results of DFT calculations for the energetic pathways present in the co-adsorption of CO and H₂O on Au₆⁺ described by the data of Figure 10. Panel (a) indicates that 2 strongly bound H₂O increase the energy barrier as well as the energy of the final structural isomer. However, as shown in panel (b), the co-adsorption of 3 chemisorbed CO molecules and 2 weakly bound H₂O results in a dramatic reduction of the energy barrier for the structural transformation, and a final structure energy reduced by ~1 eV. The pathways described in panel (c) identify the lowest energy kinetic pathway (blue arrows) leading to the experimental observation of 4 chemisorbed CO molecules on Au₆⁺. The absence of

adsorbed water on the final product is assumed to result from unimolecular desorption during the long experimental exposure at 300 K. Note in Figs. 11(b) and 11(c) that the energy required for H₂O desorption is a factor of 3 less than the energy deposited by CO adsorption.

	0 H ₂ O	1 H ₂ O	2 H ₂ O's
0 CO	0.38 eV	0.51 eV	0.55 eV
1 CO	0.53 eV	0.44 eV	0.32 eV
2 CO's	0.30 eV	0.18 eV	0.22 eV
3 CO's	0.14 eV	0.11 eV	~0.0 eV

Table 2 Adsorption Dependent Energy Barriers

Table 2 summarizes the DFT calculations of the energy barriers for CO, H₂O co-adsorption on Au₆⁺ at 300 K. In all cases, the energy barrier for >1 CO decreases with increasing CO adsorption. However, the barriers decrease significantly more strongly with the presence of adsorbed water molecules.

References

- [1] S. Krückeberg, D. Schooss, M. Maier-Borst, and J. H. Parks, *Phys. Rev. Lett.* **85**, 4494 (2000).
- [2] J. Li, X. Li, H.-J. Zhai, and L.-S. Wang, *Science* **299**, 864 (2003).
- [3] H. Häkkinen, B. Yoon, U. Landman, X. Li, H.-J. Zhai, and L.-S. Wang, *J. Phys. Chem. A* **107**, 6168 (2003).
- [4] S. Bulusu, X. Li, L.-S. Wang, and X. C. Zeng, *Proc. Natl. Acad. Sci. U.S.A.* **103**, 8326 (2006).
- [5] B. Yoon, P. Koskinen, B. Huber, O. Kostko, B. von Issendorf, H. Häkkinen, M. Moseler, and U. Landman, *Chem. Phys. Chem.* **8**, 157-161 (2007).
- [6] The term “direct structural determination method” is used here to signify a method that is based on a diffraction process, and to distinguish such method from those that while measuring properties that are structure-sensitive (for example, electron spectroscopy), are not based on scattering and/or diffraction from the atomic constituents.
- [7] X. Xing, R. M. Danell, I. L. Garzón, K. Michaelian, M. N. Blom, M. M. Burns, and J. H. Parks, *Phys. Rev. B* **72**, 081405(R) (2005).
- [8] X. Xing, B. Yoon, U. Landman, J. H. Parks, *Phys. Rev. B* **74**, 165423 (2006).
- [9] A. Sanchez, S. Abbet, U. Heiz, W.-D. Schneider, H. Häkkinen, R. N. Barnett, and U. Landman, *J. Phys. Chem. A* **103**, 9573 (1999).
- [10] H. Häkkinen, S. Abbet, A. Sanchez, U. Heiz, and U. Landman, *Angew. Chem., Int. Ed.* **42**, 1297 (2003).
- [11] B. Yoon, H. Häkkinen, U. Landman, A. S. Wörz, J.-M. Antonietti, S. Abbet, K. Judai, and U. Heiz, *Science* **307**, 403 (2005).
- [12] B. Yoon, H. Häkkinen, and U. Landman, *J. Phys. Chem. A* **107**, 4066 (2003).
- [13] DOE ESPM Contractors Meeting, Dr. Jane Zhu, Airlie Conference Center, Warrenton, VA, Oct 29-Nov1, 2006.
- [14] DOE ESPM Contractors Meeting, Dr. Jane Zhu, Airlie Conference Center, Warrenton, VA, Oct 24-28, 2008.
- [15] DOE ESPM Contractors Meeting, Dr. Jane Zhu, Airlie Conference Center, Warrenton, VA, Sept 3-5, 2010.
- [16] B.E. Salisbury, W.T. Wallace, R.L. Whetten, *Chem. Phys.* **262**, 131(2000).
- [17] S. Gilb, P. Weis, F. Furche, R. Ahlrichs, and M. M. Kappes, *J. Chem. Phys.* **116**, 4094 (2002).
- [18] F. Furche, R. Ahlrichs, P. Weis, C. Jacob, S. Gilb, T. Bierweiler, and M. M. Kappes, *J. Chem. Phys.* **117**, 6982 (2002).
- [19] M. Neumaier, F. Weigend, O. Hampe, and M. M. Kappes *J. Chem. Phys.* **122**, 104702-104702-11, (2005).
- [20] M. Neumaier, F. Weigend, O. Hampe, and M. M. Kappes *J. Chem. Phys.* **125**, 104308-104308-10, (2006).
- [21] I. Balteanu, O. P. Balaj, B. S. Fox, M. K. Beyer, Z. Bastl and V. E. Bondybey *Phys. Chem. Chem. Phys.* **5**, 1213–1218, (2003).
- [22] S. M. Lang, T. M. Bernhardt, R. N. Barnett and U. Landman *Chem. Phys. Chem* **11**, 1570-1577 (2010).
- [23] S. M. Lang, T. M. Bernhardt, R. N. Barnett, B. Yoon and U. Landman Bokwon Yoon, and U. Landman *J. Am. Chem. Soc.* **131**, 8939–8951, (2009).

- [24] T. M. Bernhardt, J. Hagen, S. M. Lang, D. M. Popolan, L. D. Socaciu-Siebert, and L. Woste J. Phys. Chem. A **113**, 2724–2733, (2009).
- [25] D. M. Popolan, M. N€ossler, R. Mitric, T. M. Bernhardt, and V. Bonacic-Koutecky J. Phys. Chem. A **115**, 951–959, (2011).
- [26] D. M. Popolan, M. N€ossler, R. Mitric, T. M. Bernhardt and V. Bonacic-Koutecky Phys. Chem. Chem. Phys. **12**, 7865–7873, (2010).
- [27] M. B. Knickelbein, Annu. Rev. Phys. Chem. **50**, 79 (1999).
- [28] M. Chen, D. Goodman, Acc. Chem. Res. **39**, 739 (2006); M. Chen, Y. Cai, Z. Yan, D. Goodman, J. Am. Chem. Soc. **128**, 6341(2006).
- [29] X. Wu, L. Senapati, S. K. Nayak, A. Selloni, M. Hajaligol, J. Chem. Phys. **117**, 4010 (2002).

Personnel

The following have worked on this program during the reporting period:

Rowland Institute:

Dr. Joel H. Parks (64% support as Rowland Senior Fellow, Harvard University)
Principal Investigator (36%)

Georgia Institute of Technology:

Dr. Bokwon Yoon Research Scientist II (40%)

Dr. Robert N. Barnett Senior Research Scientist (10 %)

Regents' Professor Uzi Landman (support through endowed Chair)

Budget: Projected unspent funds at end of current funding period- none

Current Support:

"Combustion Catalysis", AFOSR/MURI, 5/01/2008-4/30/2013 \$1,750,000 PI: U. Landman.

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The DOE grant is directed primarily to structural calculations and reactivity of supported clusters. Many aspects of that work is complementary to our experiments.

Manuscripts In Preparation

1. "Local Symmetry Mapping of Metal Clusters", Michael Burns, X. Xing and J. H. Parks.
2. "Equilibrium Adsorption of oxygen on gold cluster anions, $n=7-22$ ", X. Xing and J. H. Parks.
3. "Change in Gold Cluster Structures Induced by CO and H₂O Adsorption on Au_n⁺ $n=3-20$ ", Xi Li, X. Xing and J. H. Parks.

Invited Talks

During this subaward period invited talks which credit DOE research support include:

1. "Nanoscale Structures: Metal Cluster Isomers and Biomolecule Conformations", Graduate University of the Chinese Academy of Sciences, Beijing, China May 25, 2012.
2. "Nanoscale Structures: Metal Clusters, Reactivity and Biomolecules", Fudan University, Shanghai, China, May 28, 2012.
3. "Metal Clusters: Diffraction, Symmetry and Reactions", Tsinghua University, Beijing, China May 21, 2012.